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Synthesis, structure and ethylene polymerization behavior of zirconium complexes with chelating ketoiminate ligands

Jindong Kim, Jeong-Wook Hwang, Youngjo Kim, Min Hyung Lee, Yonggyu Han, Youngkyu Do *

Department of Chemistry, School of Molecular Science-BK21 and Center for Molecular Design and Synthesis, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

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Abstract

Mixed ketoiminate/ketoimine/pentamethylcyclopentadienyl (Cp*) complex of zirconium, [(η^5-Cp*){$CH_3C(O)CHC(NHR)CH_3$}{$CH_3C(O)CHC(NR)CH_3$}$ZrCl_2$] (R = 4-CF_3Ph) (**3**) has been prepared in high yield by the reaction of one equivalent of 4-CF_3-phenyl-β-ketoimine (**1a**) and one equivalent of lithium 4-CF_3-phenyl-β-ketoiminate (**2a**) with one equivalent of Cp*$ZrCl_3$ in Et_2O. Bis(ketoiminate)zirconium dichloride complexes, **4** and **6**, have been also prepared in high yield by the reaction of amine elimination of ketoimine ligands, respectively **1a** and **1b**, with $Zr(NMe_2)_4$ and followed by chlorination reaction with TMSCl. The X-ray crystallography reveals that the compound **3** is based on distorted octahedral geometry containing a ketoimine and a ketoiminate. The ketoiminate ligand coordinates to the zirconium as a bidentate ligand, leaving the metal center coordinatively unsaturated and thus leading to an additional binding of a ketoimine ligand to the metal to stabilize the complex **3**. The zirconium complexes **3**, **4** and **6** provide the moderate activity for the polymerization of ethylene in the presence of MMAO cocatalyst. Low molecular weight and high density polyethylene was obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; Zirconium; Ketoiminate; Ethylene; Polymerization

1. Introduction

In recent years, a considerable amount of interest has been paid in the preparation of single site polymerization catalysts based on non-Cp Group 4 complexes [1]. The majority of attempts have been made in developing new systems analogous to Group 4 metallocene complexes that have been extensively studied because of their high activity in olefin polymerization [2]. For this purpose, a number of non-Cp ligands such as bulky alkoxides [3], amides [4], tetradentate Schiff bases [5], keteniminates [6] and amidinates [7] have been employed. Anionic ketoiminate ligands $[CH_3C(O)CHC(NR)CH_3]^{n-}$ ($n = 2$ for R = $-CH_2CH_2O$ [8a]; $n = 1$ for R = Ph [8b]), another potential isoelectronic alternatives to cyclopentadienyl anion owing to their chelating ability, planar skeleton and resonance driven high acidity, have been also utilized in preparing titanium or zirconium complexes of the hetero- or homoleptic type, but their catalytic behavior toward the olefin polymerization has not been reported [8]. Therefore, new ketoiminate ligands and their zirconium complexes have been synthesized in order to confirm the use of ketoiminate as a non-Cp ancillary ligand in the preparation of Group 4 olefin polymerization catalyst. Reported herein are the syntheses, structures and ethylene polymerization of mixed ketoiminate/Cp* complex of zirconium, [(η^5-Cp*){$CH_3C(O)CHC(NHR)CH_3$}{$CH_3C(O)CHC(NR)CH_3$}$ZrCl_2$] (R = 4-CF_3Ph) (**3**), and bis(ketoiminate)zirconium dichloride complexes, {$CH_3C(O)CHC(NR)CH_3$}$_2ZrCl_2$ {R = 4-CF_3Ph (**4**) and R = 2,6-(CH3)2Ph (**6**)}.

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* Corresponding author. Fax: + 82-42-869-2810.
E-mail address: ykdo@mail.kaist.ac.kr (Y. Do).

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2. Experimental

2.1. General procedure

All operations were performed under dinitrogen atmosphere by using conventional Schlenk-line glovebox techniques. Toluene and hexane were distilled from Na–K alloy; Et$_2$O was distilled from Na-benzophenone ketyl. CDCl$_3$ was dried over activated molecular sieves (4 Å) and then vacuum transferred to Schlenk tube equipped with a J. Young valve. Methylalumoxane (Akzo, type 4) modified with an isobutyl group was purchased as a toluene solution. Other chemicals were used without any further purification after purchasing from Aldrich (2,4-pentadione, 4-trifluoroaniline, TMSCl and n-BuLi) and Strem (Cp*ZrCl$_3$ and Zr(NMe$_2$)$_4$). The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AC 200 and Bruker Avance 400 spectrometers at ambient temperature. Elemental analyses were performed with an EA 1110-FISONS instrument (CE instruments) at KAIST. Molecular weights and molecular weight distributions of the polymers were determined by GPC (Waters 150C, 130°C) in 1,2,4-trichlorobenzene using polystyrene columns as a standard.

*2.2. Preparation of [CH$_3$C(O)CHC(NHR)CH$_3$] (R = 4-CF$_3$Ph) (**1a**)*

A solution of 2,4-pentadione (5.1 g, 51.0 mmol) in toluene was added to a solution of 4-trifluoroaniline (8.2 g, 51.0 mmol) and catalytic trace of p-toluenesulfonic acid in toluene, and then the mixture was refluxed with Dean–Stock apparatus to remove water for 12 h. The resulting solution was extracted with Et$_2$O–water and the Et$_2$O layer was dried with anhydrous MgSO$_4$ and evaporated under the vacuum. The resulting residue was yellow solid (12 g, 96%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ12.57 (s, 1H, NH), 7.48 (d, 2H, m-C$_6H_4$CF$_3$), 7.09 (s, 2H, o-C$_6H_4$CF$_3$), 5.18 (s, 1H, CH), 2.03 (s, 3H, CHCOCH_3), 1.98 (s, 3H, CHCNCH_3). ^{13}C{^{1}H}-NMR (400 MHz, CDCl$_3$): δ169.90, 158.44, 142.17, 123.97(q, $J_{CF} = 1080.35$), 126.46 (q, $J_{CCF} = 128.04$), 126.21 (d, $J_{CCCF} = 13.60$), 123.24, 99.24, 29.14, 19.86.

*2.3. Preparation of [CH$_3$C(O)CHC(NHR)CH$_3$] (R = 2,6-(CH$_3$)$_2$Ph) (**1b**)*

The desired product was prepared by the reaction of 2,4-pentadione (5.1 g, 51.0 mmol) and 2,6-dimethylaniline (6.2 g, 51.0 mmol) in the manner analogous to the procedure for **1a**. The resulting residue was yellow solid (9.7 g, 95%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ11.89 (s, 1H, NH), 6.99 (m, 3H, Ph), 5.14 (s, 1H, CH), 2.11 (s, 3H, 2,6-(CH_3)$_2$Ph), 2.02 (s, 3H, CHCNCH_3), 1.53 (s, 3H, CHCNCH_3). ^{13}C{^{1}H}-NMR (400 MHz, CDCl$_3$): δ195.40, 162.27, 136.08, 135.58, 127.78, 127.74, 127.00, 95.38, 28.60, 18.38, 17.78.

*2.4. Preparation of [CH$_3$C(O)CHC(NLiR)CH$_3$] (R = 4-CF$_3$Ph) (**2a**)*

Ketoimine **1a** (3.0 g, 12.3 mmol) in hexane (100 ml) was added to a 250 ml flask equipped with a magnetic stirrer. The solution was cooled to −78°C, and then n-BuLi (5.4 ml, 2.5 M) in hexane was added dropwise. The reaction mixture was warmed to room temperature (r.t.) and stirred overnight. The resulting yellow solution over a pale yellow precipitate was decanted off and the solid was washed with hexane. Drying in a vacuum afforded 2.6 g (84%) of the pale yellow powder product **2a**. ^{1}H-NMR (200 MHz, 5:1, C$_6$D$_6$–THF-d_8): δ 7.38 (d, 2H, m-C$_6H_4$CF$_3$), 6.70 (d, 2H, o-C$_6H_4$-CF$_3$), 4.92 (s, 1H, CH), 1.69 (s, 3H, CHCOCH_3), 1.56 (s, 3H, CHCNCH_3).

2.5. Preparation of [(Cp){CH$_3$C(O)CHC(NR)CH$_3$}-{CH$_3$C(O)CHC(NHR)CH$_3$}-ZrCl$_2$] (R = 4-CF$_3$Ph) (**3**)*

A solution of ketoiminate **2a** (0.37 g, 1.50 mmol) and ketoimine **1a** (0.37 g, 1.50 mmol) in Et$_2$O (30 ml) was added to a solution of Cp*ZrCl$_3$ (0.50 g, 1.50 mmol) in Et$_2$O (50 ml) at −78°C dropwise. After the reaction mixture was warmed to r.t. and stirred for 12 h, all volatiles were removed by drying in vacuum. The resulting residue was extracted with toluene and filtered through Celite pad. The extract was condensed and added hexane and then cooled at −20°C to give a yellow crystal (0.86 g, 73%). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 10.49 (s, 1H, NH), 7.70 (d, 2H, m-C$_6H_4$CF$_3$), 7.43 (d, 2H, m-C$_6H_4$CF$_3$), 7.36 (s, 2H, o-C$_6H_4$CF$_3$), 7.29 (d, 2H, o-C$_6H_4$CF$_3$), 5.21 (s, 1H, CH), 4.71 (s, 1H, CH), 1.93 (s, 3H, CHCOCH_3), 1.92 (s, 3H, CHCNCH_3), 1.88 (s, 15H, Cp*), 1.83 (s, 3H, CHCOCH_3), 1.49 (s, 3H, CHCNCH_3). ^{13}C{^{1}H}-NMR (400 MHz, CDCl$_3$): δ 195.04, 171.25, 167.21, 164.61, 155.52, 140.31, 130.06 (q, 1C, $J_{\mathrm{CCF}} = 0.328$, ketoiminate), 126.95 (s, 2C, o-C_6H$_4$CF$_3$ of ketoimine), 126.29 (q, 1C, $J_{\mathrm{CCF}} = 0.321$, ketoimine), 126.39 (q, 2C, $J_{\mathrm{CCCF}} = 0.037$, ketoimine), 125.98 ($s$, 1C, o-C_6H$_4CF_3$ of ketoiminate), 125.28 (q, $J_{\mathrm{CCCF}} = 0.037$, ketoiminate), 125.04 ($s$, 1C, o-C_6H$_4CF_3$ of ketoiminate), 124.55(q, $J_{\mathrm{CCCF}} = 0.037$, ketoiminate), 124.49 ($s$, 5C, C(CH3) of Cp*), 124.41 (q, 1C, $J_{\mathrm{CF}} = 2.698$, ketoiminate), 123.66 (q, 1C, $J_{\mathrm{CF}} = 2.705$, ketoimine), 103.08, 100.52, 27.55, 25.45, 25.26, 21.19, 12.32. Anal. Calc. for C$_{34}$H$_{38}$-Cl$_2$F$_6$N$_2$O$_2$Zr: C, 52.17; H, 4.89; N, 3.58. Found: C, 52.93; H, 4.65; N, 3.83%.

2.6. Preparation of $\{CH_3C(O)CHC(NR)CH_3\}_2ZrCl_2]$ ($R = 4\text{-}CF_3Ph$) (**4**)

A solution of ketoimine **1a** (0.75 g, 3.10 mmol) in toluene (30 ml) was added to a solution of $Zr(NMe_2)_4$ (0.40 g, 1.50 mmol) in toluene (50 ml) at − 78°C. After the reaction mixture was warmed to r.t. and stirred for 12 h, all volatiles were removed by drying in vacuum. The resulting yellow solid was re-dissolved in toluene for the further reaction without purification. TMSCl (0.43 g, 4.00 mmol) was added to the solution at − 78°C. After the reaction mixture was warmed to r.t. and stirred for 12 h, all volatiles were removed by drying in vacuum and carefully washed with hexane. The resulting residue was extracted with toluene and filtered through Celite pad. Removal of solvent gives desired product as a pale yellow powder (0.83 g, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 8H, $C_6H_4CF_3$), 5.31 (s, 2H, C*H*), 1.73 (s, 6H, $CHCOCH_3$), 1.31 (s, 6H, $CHCNCH_3$). $^{13}C\{^1H\}$-NMR (400 MHz, $CDCl_3$): δ 175.68, 173.29, 151.81, 128.16 (*q*, 2C, $J_{CCF} = 0.33$), 126.09 (*q*, 4C, $J_{CCCF} = 0.03$), 125.26 (*s*, 4C, *o*-$C_6H_4CF_3$), 123.91 (*q*, 2C, $J_{CF} = 2.71$), 106.40, 24.84, 22.68. Anal. Calc. for $C_{24}H_{22}Cl_2F_6N_2O_2Zr$: C, 44.58; H, 3.43; N, 4.33. Found: C, 44.12; H, 4.40; N, 4.00%.

2.7. Preparation of $\{CH_3C(O)CHC(NR)CH_3\}_2Zr(NMe_2)_2$ ($R = 2,6\text{-}(CH_3)_2Ph$) (**5**)

A solution of ketoimine **1b** (0.63 g, 3.10 mmol) in toluene (30 ml) was added to a solution of $Zr(NMe_2)_4$ (0.40 g, 1.50 mmol) in toluene (50 ml) at − 78°C. After the reaction mixture was warmed to r.t. and stirred for 12 h, all volatiles were removed by drying in vacuum. The resulting residue was extracted with toluene and filtered through Celite pad. The extract was condensed and added hexane and then cooled at − 20°C to give a pale yellow crystal. (0.72 g, 82%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 (d, 2H, $(CH_3)_2Ph$), 7.02 (d, 2H, $(CH_3)_2Ph$), 6.93 (d, 2H, $(CH_3)_2Ph$), 5.10 (s, 1H, C*H*), 2.51 (br, 12H, NMe_2), 2.49 (s, 6H, $(CH_3)_2Ph$), 2.16 (s, 6H, $(CH_3)_2Ph$), 1.91 (s, 6H, CCH_3), 1.47 (s, 6H, CCH_3). $^{13}C\{^1H\}$-NMR (400MHz, $CDCl_3$): δ 177.54, 170.72, 149.83, 132.30, 131.11, 129.27, 128.91, 128.50, 125.64, 124.51, 101.44, 44.48, 25.27, 23.32, 18.81, 17.83.

2.8. Preparation of $\{CH_3C(O)CHC(NR)CH_3\}_2ZrCl_2$ ($R = 2,6\text{-}(CH_3)_2Ph$) (**6**)

TMSCl (0.28 g, 2.58 mmol) was added to a solution of ketoimine **5** (0.50 g, 0.86 mmol) in toluene (30 ml) at − 78°C. After the reaction mixture was warmed to r.t. and stirred for 12 h, all volatiles were removed by drying in vacuum and carefully washed with hexane. The resulting residue was extracted with CH_2Cl_2 and filtered through Celite pad. The extract was condensed and added hexane and then cooled at − 20°C to give a pale yellow solid. (0.42 g, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 6H, $(CH_3)_2Ph$), 5.61 (s, 1H, C*H*), 2.25 (s, 12H, $(CH_3)_2Ph$), 1.94 (s, 6H, CCH_3), 1.70 (s, 6H, CCH_3). $^{13}C\{^1H\}$-NMR (400MHz, $CDCl_3$): δ 175.53, 174.67, 146.26, 128.60, 128.13, 126.07, 23.52, 23.34, 18.85. Anal. Calc. for $C_{26}H_{32}Cl_2N_2O_2Zr$: C, 55.11; H, 5.69; N, 4.94. Found: C, 54.86; H, 6.02; N, 4.77%.

2.9. Ethylene polymerization

Polymerizations were carried out in a 250 ml Schlenk flask with magnetic stirring. The flask was filled with 50 ml of toluene and the solvent saturated with ethylene monomer at 1 atm. The catalyst solution was prepared externally by dissolving in toluene and injected into the stirred reaction solution. And then MMAO co-catalyst dissolved in toluene was injected into the reaction solution. Simultaneous closing of the ethylene valve and injection of methanol into the reaction flask terminated the polymerization reaction. The reaction solution was poured into the excess 10% HCl–MeOH, affording polyethylene as a suspended precipitate. The polymer was filtered and washed with MeOH several times and dried in vacuum at 50°C for 12 h.

2.10. X-ray structure determination

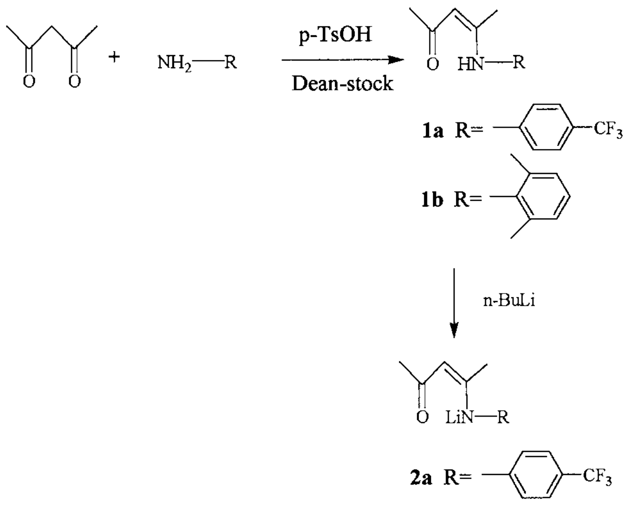
A single crystal suitable for X-ray structure determination was sealed in a thin wall glass capillary under an argon atmosphere. The measurements of diffraction intensity were carried out on an Enraf-Nonius CAD4TSB diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at 293 K. Accurate unit cell parameters and orientation matrix were determined from the least-squares fit of 25 accurately centered reflections in the range of $11.25° < 2\sigma < 26.69°$. Intensity data were collected by using the ω–2θ scan mode with a range of $1 < \theta < 25°$. All the intensity data were corrected for Lorentz and polarization effects. The structure was solved by semi-invariant direct methods (SIR-92 in MOLEN) and refined by full-matrix least-squares refinement (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at $R_1 = 0.0718$, $wR_2 = 0.1653$ and GoF = 1.085. All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data are given in Table 1.

Table 1
Crystallographic data and parameters for **3**

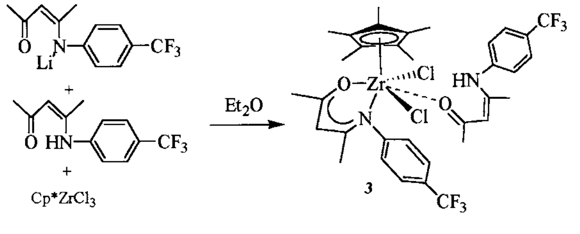
Formula	$C_{34}H_{38}Cl_2F_6N_2O_2Zr$
Formula weight	782.81
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
Unit cell dimensions	
a (Å)	15.776(2)
b (Å)	17.484(3)
c (Å)	25.825(9)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	7123(3)
Z	8
$D_{(calc)}$ (g cm^{-3})	1.460
F (000)	3200
T (K)	293
μ (Mo–K$_\alpha$) (cm^{-1})	5.2
Scan mode	ω–2θ
θ Range (°)	1; 25
No. of unique reflections	5015
No. of observed reflections ($I > 2\sigma(I)$)	3333
No. of parameters refined	437
[a]R_1	0.0718
[b]wR_2	0.1653
GoF	1.08500
Max. residual density (e Å^{-3})	0.891

[a] $R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$.



Scheme 1.



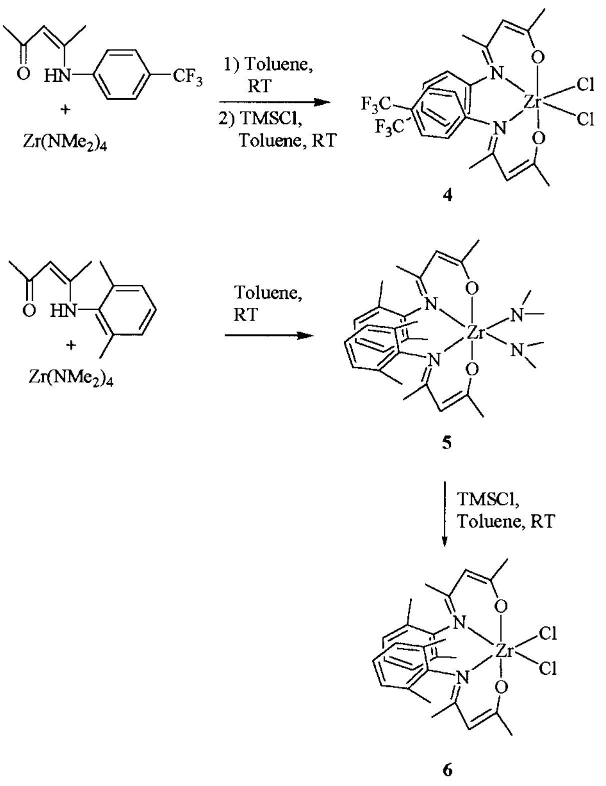
Scheme 2.

3. Results and discussion

3.1. Synthesis

The preparation routes to the ketoimine (**1a**,**b**) and ketoiminate (**2a**) ligands utilized in this work are shown in Scheme 1. The Dean–Stock reaction of 2,4-pentadione with substituted aniline in toluene turned out useful in the synthesis of the ketoimine ligands, **1a** and **1b**, in high yield. The ketoimine fragments are expected to be planar due to the resonance between oxygen and nitrogen through the double bond conjugation. The acidity of the ligand is increased by the electron-withdrawing CF_3 functional group. These two features are reflected in the ^{1}H-NMR spectrum of the ligand **1a** as seen by a broad singlet at δ 12.56 ppm. The lithium salt of ketoiminate ligand, **2a**, was obtained by the reaction of *n*-BuLi with the ligand **1a** in hexane.

The synthesis of the mixed ketoiminate/ketoimine/Cp* complex **3** is rather unusual in a sense that the reaction of **2a** with Cp^*ZrCl_3 in Et_2O in equimolar ratio produces an ill-defined complex mixture of products containing a little amount of **3** instead of the attempted yet unknown complex [(4-CF_3-phenylketoiminate)Cp^*ZrCl_2], suggesting the possible role of the ketoimine ligand in stabilizing [(4-CF_3-phenylketoiminate)Cp^*ZrCl_2]. In fact, the equimolar reaction of **2a** with Cp^*ZrCl_3 in Et_2O in the presence of the ketoimine ligand **1a** gave **3** in high yield (Scheme 2). The complex **3** is soluble in toluene, CH_2Cl_2 and THF.



Scheme 3.

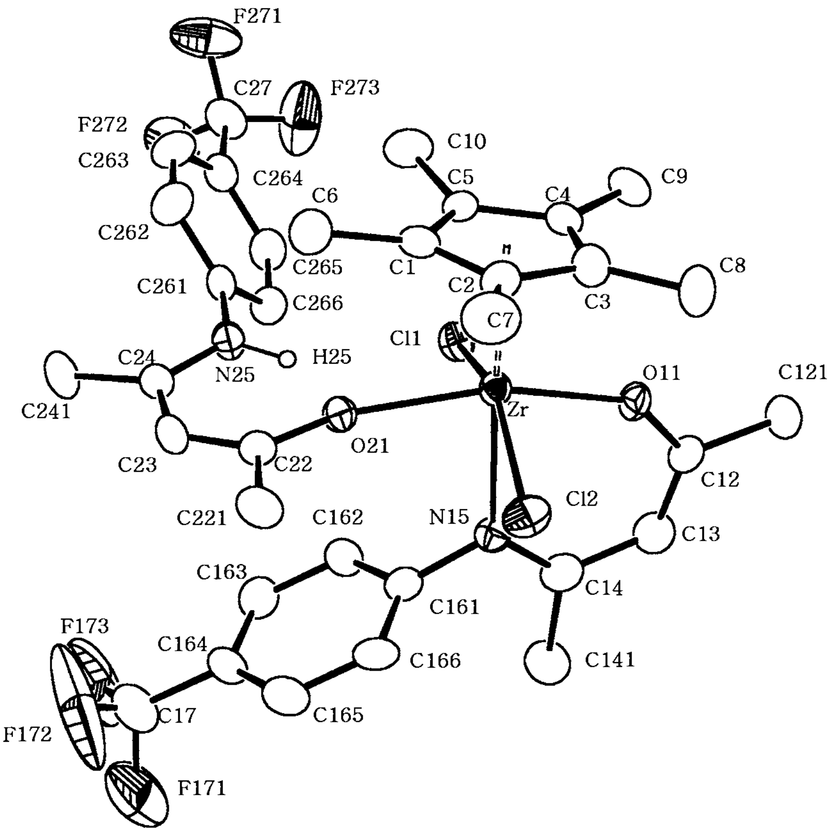


Fig. 1. Molecular structure of **3** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The bis(ketoiminate)zirconium dichloride complexes, **4** and **6**, were prepared in high yield by the reaction of amine elimination of ketoimine ligands, respectively **1a** and **1b**, with $Zr(NMe_2)_4$ and followed by chlorination reaction with TMSCl. The preparation routes are shown in Scheme 3. The bis(ketoiminate) zirconium dichloride complexes have five possible octahedral structures. The general structural trends of zirconium complexes of bis [N,O] bidentate ligands, $[N,O]_2ZrX_2$, have been investigated in a few works and can be summarized such that two oxygen are favored by the *trans* orientation to each other, two nitrogen are favored by the *cis* orientation and two monodentate ligands, X, such as chloride, amide and alkyl are also favored by the *cis* orientation [8b,10].

3.2. Solid-state structure of 3

A single crystal was obtained from toluene–hexane solution at −20°C. An ORTEP view is shown in Figs. 1 and 2, and crystallographic details and selected bond distances and angles are listed in Table 2. The zirconium metal of the complex **3** adopts a distorted octahedral geometry. Among three *trans* components, only the angle of N15–Zr–Cp* centroid is nearly linear with 176.8° and the other two *trans* components Cl1–Zr–Cl2 and O11–Zr–O21 are bent away from the Cp* plane. The plane of O11–C12–C13–C14–N15 of ketoiminate bisects the Cl–Zr–Cl angle, includes the bond between Zr and the centroid of Cp*, and is nearly perpendicular to the planes of Cp* and the phenyl ring of the ketoiminate with the dihedral angles of 89.5(3)°

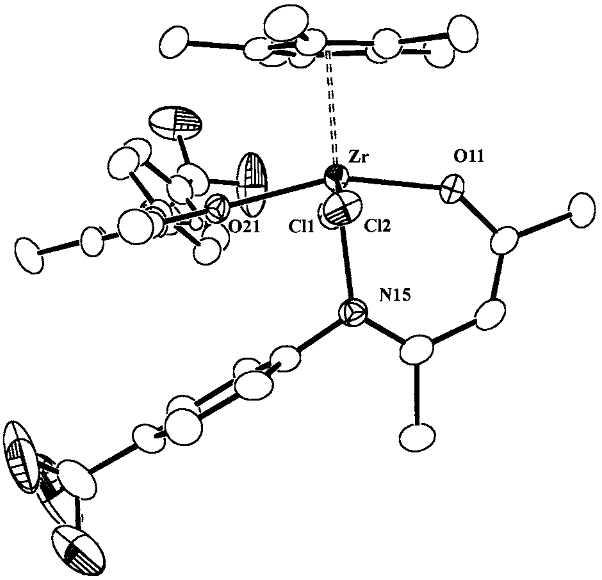


Fig. 2. Side view of **3** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for **3**

Bond distances			
Zr–Cl(1)	2.547(2)	Zr–Cl(2)	2.508(2)
Zr–O(11)	2.054(5)	Zr–O(21)	2.166(5)
Zr–N(15)	2.418(6)	Zr–Cp*[a]	2.602(8)
O(11)–C(12)	1.314(10)	O(21)–C(22)	1.291(9)
C(12)–C(13)	1.342(12)	C(22)–C(23)	1.374(11)
C(13)–C(14)	1.445(13)	C(23)–C(24)	1.402(11)
N(15)–C(14)	1.303(11)	N(25)–C(24)	1.333(10)
N(15)–C(161)	1.441(11)	N(25)–C(261)	1.434(11)
O(21)–H(25)	2.072	N(25)–H(25)	0.92(8)
Cl(1)–H(25)	2.573		
Bond angles			
Cl(1)–Zr–Cl(2)	152.86(8)	N(15)–Zr–Cp* [a]	176.83
Cl(1)–Zr–O(11)	86.49(15)	Cl(2)–Zr–O(11)	90.51(16)
Cl(1)–Zr–O(21)	82.67(14)	Cl(2)–Zr–O(21)	90.85(15)
Cl(1)–Zr–N(15)	75.97(19)	Cl(2)–Zr–N(15)	77.05(19)
O(11)–Zr–N(15)	77.3(2)	O(21)–Zr–N(15)	82.3(2)
Zr–N(15)–C(161)	117.3(5)	O(11)–Zr–O(21)	158.73(19)

[a] Cp*, centroid of C(1,2,3,4,5) of Cp*.

and 89.0(3)°, respectively. The planes of Cp* and the phenyl ring of the ketoiminate form a dihedral angle of 28.9(4)°. The neutral 4-CF_3-phenyl-β-ketoimine ligand is strongly [9] coordinated to zirconium via the carbonyl oxygen, O21. This oxygen is involved to form a hydrogen bonding with the imine hydrogen H25 as indicated by the O21–H25 distance of 2.072 Å. Unlike the ketoiminate ligand, the ketoimine ligand does not adopt orthogonality between the phenyl ring of C261 ~ C266 and the plane of O21–C22–C23–C24–N25 whose dihedral angle is 62.2(4)°. The Zr–Cl bonding interactions (2.547(2) and 2.508(2) Å) in the complex **3** are not symmetric. The bonding interactions within the ketoiminate ligand are localized as evidenced by the difference of 0.103 Å between the bond lengths of C12–C13 and C13–C14 compared to the difference of 0.028 and 0.004 Å for the comparable bond lengths in the additional ketoimine ligand of the complex **3** and the bis(keteniminate)zirconiumdichloride complex, $[Zr\{CH_3C(NPh)CHC(NPh)CH_3\}_2ZrCl_2]$ [6b], respectively.

Table 3
Ethylene polymerization using **3** [a]

Entry	Catalyst	T (°C)	A [b]	T_m	M_n	M_w	M_w/M_n
1	**3**	50	28.4	134.5	21 700	36 520	6.8
2	**3**	70	124.7	134.3	17 200	109 000	6.3
3	**3**	90	99.4	132.7	11 300	53 200	4.7
4 [c]	**3**	70	188.8	132.2	8280	34 000	4.1
5	**4**	70	6.5	132.4	–	–	–
6	**6**	70	4.8	132.2	–	–	–
7	Cp^*ZrCl_3	70	163.1	132.0	13 600	64 300	4.7

[a] Conditions: toluene (50 ml), catalyst = 10 μmol, Al/Zr = 1000, C_2H_4 = 1 atm, time = 1 h unless otherwise noted.

[b] Activity: kg PE (mol of cat.·h·atm)$^{-1}$.

[c] Al/Zr = 2000.

In contrast to the η^5-coordination mode of the keteniminate ligand in the mixed (keteniminate)-(indenyl)$ZrCl_2$ complex, $[Zr\{CH_3C(PhN)CHC(NPh)CH_3\}(C_9H_7)Cl_2]$, and (keteniminate)$ZrCl_3$ complex [6b,d,e], the ketoiminate of the complex **3** acts only as a bidentate ligand, making Zr coordinatively unsaturated. Therefore, the additional binding of the ketoimine ligand to the Zr center would stabilize the complex **3**, leading to its isolation.

3.3. Ethylene polymerization

The complex **3** when activated by modified methylaluminoxane (MMAO) shows moderate catalytic activity for the ethylene polymerization. On the other hand, bis(ketoiminate)zirconium dichloride complexes, **4** and **6**, show very low activity under the same conditions with complex **3**. The effect of polymerization temperature on the catalyst activity has been evaluated in the temperature range of 50 ~ 90°C, at Al/Zr = 1000. A summary of the polymerization results is given in Table 3. The catalytic activity of the complex **3** increases as the reaction temperature increases and reaches a maximum at 70°C. However the molecular weight of the polymer obtained in the range of reaction temperature 50 ~ 90°C decreases as the temperature increases. Molecular weight and molecular weight distribution (MWD) measured by GPC in 1,2,4-trichlorobenzene using polystyrene columns as a standard show that relatively low and broad molecular weight polyethylene was obtained under the polymerization conditions. Melting temperatures measured by differential scanning calorimeter (DSC) are typical of high-density polyethylene. The catalytic activity and the molecular weight of the polymer derived from the complex **3** are similar to those of Cp^*ZrCl_3.

4. Conclusion

The mixed Cp*(ketoiminate)(ketoimine) complex of zirconium **3** was prepared in a high yield by the reaction of ketoimine and ketoiminate with Cp*ZrCl3 and characterized by X-ray crystallography. The role of the ketoimine ligand in stabilizing the complex **3** was explained in terms of filling a coordination vacancy formed by a bidentate binding mode of the ketoiminate ligand. The catalytic behavior evaluated by the ethylene polymerization shows that the complex **3** is moderate active. The polymers obtained by the polymerization reaction were characterized as having low molecular weight and high density.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144002 for **3.** Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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